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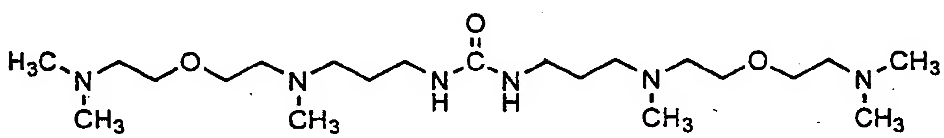
(54) N,N,N'-Trimethylbis (aminoethyl)-ether substituted urea compositions for the production of polyurethanes

(57) A method for preparing a polyurethane foam which comprises reacting an organic polyisocyanate and a polyol in the presence of a blowing agent, a cell stabilizer and a catalyst composition consisting essentially of the compound represented by the following formula I or II, or any blend of I and II.



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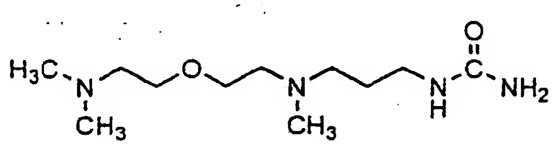

II

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Description

BACKGROUND OF THE INVENTION

The present invention relates to the use of tertiary amine catalysts for producing polyurethanes, especially polyurethane foam.

Polyurethane foams are widely known and used in automotive, housing and other industries. Such foams are produced by reaction of a polyisocyanate with a polyol in the presence of various additives. One such additive is a chlorofluorocarbon (CFC) blowing agent which vaporizes as a result of the reaction exotherm, causing the polymerizing mass to form a foam. The discovery that CFCs deplete ozone in the stratosphere has resulted in mandates diminishing CFC use. Production of water-blown foams, in which blowing is performed with CO_2 generated by the reaction of water with the polyisocyanate, has therefore become increasingly important. Tertiary amine catalysts are typically used to accelerate blowing (reaction of water with isocyanate to generate CO_2) and gelling (reaction of polyol with isocyanate).

The ability of the tertiary amine catalyst to selectively promote either blowing or gelling is an important consideration in selecting a catalyst for the production of a particular polyurethane foam. If a catalyst promotes the blowing reaction to a too high degree, much of the CO_2 will be evolved before sufficient reaction of isocyanate with polyol has occurred, and the CO_2 will bubble out of the formulation, resulting in collapse of the foam. A foam of poor quality will be produced. On the other hand, if a catalyst too strongly promotes the gelling reaction, a substantial portion of the CO_2 will be evolved after a significant degree of polymerization has occurred. Again, a poor quality foam, this time characterized by high density, broken or poorly defined cells, or other undesirable features, will be produced.

Tertiary amine catalysts generally are malodorous and offensive and many have high volatility due to low molecular weight. Release of tertiary amines during foam processing may present significant safety and toxicity problems, and release of residual amines from consumer products is generally undesirable.

Amine catalysts which contain ureido functionality (e.g., $CONH_2$) have an increase in molecular weight and hydrogen bonding and reduced volatility and odor when compared to related structures which lack this functionality. Furthermore, catalysts which contain ureido functionality chemically bond into the urethane during the reaction and are not released from the finished product. Catalyst structures which embody this concept are typically of low to moderate activity and promote both the blowing (water-isocyanate) and the gelling (polyol-isocyanate) reactions to varying extents.

U.S. 4,644,017 discloses the use of certain diffusion stable amino alkyl ureas having tertiary amino groups in the production of a polyisocyanate addition product which do not discolor or change the constitution of surrounding materials such as PVC.

U.S. 4,007,140 discloses the use of N,N'-bis(3-dimethylaminopropyl)urea as a low odor catalyst for the manufacture of polyurethanes.

U.S. 4,194,069 discloses the use of N-(3-dimethylaminopropyl)-N'-(3-morpholinopropyl)urea, N,N'-bis(3-dimethylaminopropyl)urea and N,N'-bis(3-morpholinopropyl)urea as catalysts for producing polyurethanes.

U.S. 4,094,827 discloses the use of certain alkyl substituted ureas which provide lower odor and a delay in the foaming reaction that aids in the production of polyurethane foam.

U.S. 4,330,656 discloses the use of N-alkyl ureas as catalysts for the reaction of 1,5-napthylene diisocyanate with polyols or for the chain extension of prepolymers based upon 1,5-napthylene diisocyanate without accelerating atmospheric oxidation.

DE 30 27 796 A1 discloses the use of higher molecular weight dialkyl aminoalkyl ureas as reduced odor catalysts for the production of polyurethane foam.

SUMMARY OF THE INVENTION

The present invention provides a composition for catalyzing the trimerization of an isocyanate and/or the reaction between an isocyanate and a compound containing a reactive hydrogen, e.g.,the blowing reaction and the urethane reaction for making polyurethane. The catalyst composition comprises an N,N,N'-trimethylbis(aminoethyl)ether substituted urea represented by formula I or II:

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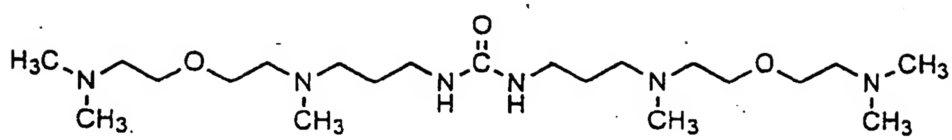

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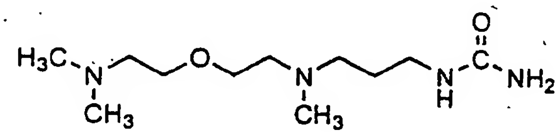

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The catalyst composition may comprise compound I, compound II, or a blend of compounds I and II in any weight ratio.

The advantage of these catalyst compounds is their high activity and blowing selectivity. Additionally, they contain a ureido group which will react with isocyanate and chemically bond into the urethane during the reaction; therefore, the catalyst composition is not released from the finished product. The compositions are somewhat viscous and have minimal odor.

DETAILED DESCRIPTION OF THE INVENTION

The catalyst compositions according to the invention can catalyze (1) the reaction between an isocyanate functionality and an active hydrogen-containing compound, i.e. an alcohol, a polyol, an amine or water, especially the urethane (gelling) reaction of polyol hydroxyls with isocyanate to make polyurethanes and the blowing reaction of water with isocyanate to release carbon dioxide for making foamed polyurethanes, and/or (2) the trimerization of the isocyanate functionality to form polyisocyanurates.

The polyurethane products are prepared using any suitable organic polyisocyanates well known in the art including, for example, hexamethylene diisocyanate, phenylene diisocyanate, toluene diisocyanate ("TDI") and 4, 4'-diphenylmethane diisocyanate ("MDI"). Especially suitable are the 2,4- and 2,6-TDI's individually or together as their commercially available mixtures. Other suitable isocyanates are mixtures of diisocyanates known commercially as "crude MDI", also known as PAPI, which contain about 60% of 4,4'-diphenylmethane diisocyanate along with other isomeric and analogous higher polyisocyanates. Also suitable are "prepolymers" of these polyisocyanates comprising a partially prereacted mixture of a polyisocyanate and a polyether or polyester polyol.

Illustrative of suitable polyols as a component of the polyurethane composition are the polyalkylene ether and polyester polyols. The polyalkylene ether polyols include the poly(alkylene oxide) polymers such as poly(ethylene oxide) and poly(propylene oxide) polymers and copolymers with terminal hydroxyl groups derived from polyhydric compounds, including diols and triols; for example, among others, ethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, diethylene glycol, dipropylene glycol, pentaerythritol, glycerol, diglycerol, trimethylol propane and like low molecular weight polyols.

In the practice of this invention, a single high molecular weight polyether polyol may be used. Also, mixtures of high molecular weight polyether polyols such as mixtures of di- and trifunctional materials and/or different molecular weight or different chemical composition materials may be used.

Useful polyester polyols include those produced by reacting a dicarboxylic acid with an excess of a do, for example, adipic acid with ethylene glycol or butanediol, or reacting a lactone with an excess of a diol such as caprolactone with propylene glycol.

In addition to the polyether and polyester polyols, the masterbatches, or premix compositions, frequently contain a polymer polyol. Polymer polyols are used in polyurethane foam to increase the foam's resistance to deformation, i.e. to increase the load-bearing properties of the foam. Currently, two different types of polymer polyols are used to achieve load-bearing improvement. The first type, described as a graft polyol, consists of a triol in which vinyl monomers are graft copolymerized. Styrene and acrylonitrile are the usual monomers of choice. The second type, a polyurea modified polyol, is a polyol containing a polyurea dispersion formed by the reaction of a diamine and TDI. Since TDI is used in excess, some of the TDI may react with both the polyol and polyurea. This second type of polymer polyol has a variant called PIPA polyol which is formed by the in-situ polymerization of TDI and alkanolamine in the polyol. Depending on

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the load-bearing requirements, polymer polyols may comprise 20-80% of the polyol portion of the masterbatch.

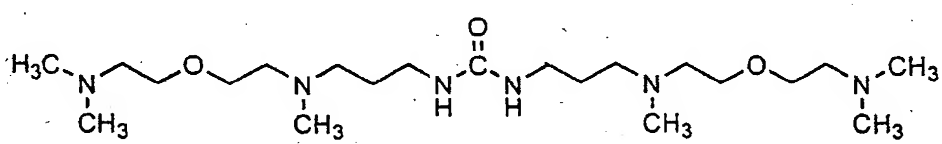
Other typical agents found in the polyurethane foam formulations include chain extenders such as ethylene glycol and butanediol; crosslinkers such as diethanolamine, diisopropanolamine, triethanolamine and tripropanolamine; blowing agents such as water, CFCs, HCFCs, HFCs, pentane, and the like; and cell stabilizers such as silicones.

A general polyurethane flexible foam formulation having a 1-3 lb/ft^3 (16-48 kg/m^3) density (e.g., automotive seating) containing a gelling catalyst such as triethylenediamine (TEDA) and a blowing catalyst such as the catalyst composition according to the invention would comprise the following components in parts by weight (pbw):

Flexible Foam Formulation	pbw
Polyol	20-100
Polymer Polyol	80-0
Silicone Surfactant	1-2.5
Blowing Agent	2-4.5
Crosslinker	0.5-2
Catalyst	0.2-2
Isocyanate Index	70-115

Any gelling catalyst known in the polyurethane art may be used with the catalyst compounds of the invention. Illustrative of suitable gelling catalysts are TEDA and tin urethane catalysts.

The blowing catalyst composition comprises the compounds represented by the following formulas **I** and **II**, and any wt% combination of compounds **I** and **II**. Mixtures of compounds **I** and **II** may comprise 50 to 95 wt% compound **I** and 5 to 50 wt% compound **II**. As a result of the preparation procedure the catalyst composition may also contain up to 20 wt% unreacted urea **III**.



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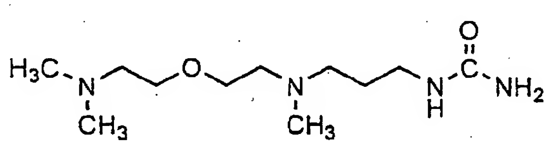

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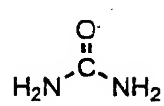

III

Compounds I and II are prepared by reacting urea and 4,10-diaza-4,10,10-trimethyl-7-oxa-undecanamine in the appropriate molar ratios under an inert atmosphere at elevated temperatures. Compounds I and II can be isolated individually by chromatography.

A catalytically effective amount of the catalyst composition is used in the polyurethane formulation. More specifically, suitable amounts of the catalyst composition may range from about 0.01 to 10 parts by wt per 100 parts polyol

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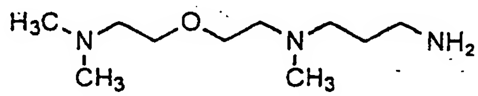
(phpp) in the polyurethane formulation, preferably 0.05 to 0.5 phpp.

The catalyst composition may be used in combination with, or also comprise, other tertiary amine, organotin or carboxylate urethane catalysts (gelling and/or blowing) well known in the urethane art.

EXAMPLE 1

Blend of 4,10-Diaza-4,10,10-trimethyl-7-oxa-undecane urea and N,N'-Bis-(4,10-diaza-4,10,10-trimethyl-7-oxa-undecane) urea

A one liter 3 neck round bottom flask was fitted with the following: mechanical stirrer, reflux condenser, nitrogen sparger, and a temperature controlled heating mantle. The flask was charged with 138.31 g of urea (CH_4N_2O) and 467.49 g of 4,10-diaza-4,10,10-trimethyl-7-oxa-undecanamine (IV) ($C_{10}H_{25}N_3O$). (Compound IV can be prepared according to following Examples 5-7.)



IV

The mixture was stirred at a constant rate while being slowly heated to 120°C. The reaction was controlled at 120°C until all signs of NH_3 evolution had ceased (as evidenced by bubbling in the N_2 pressure relief device). The pale yellow liquid was cooled to 80°C and the flask containing the liquid was evacuated via vacuum pump and refilled with N_2 three time to remove any volatiles still present. Table 1 presents quantitative ^{13}C NMR analysis of the reaction.

Table 1

Reaction Product Example 1	mole %
4,10-Diaza-4,10,10-trimethyl-7-oxa-undecane urea	85.27
N,N'-Bis-(4,10-diaza-4,10,10-trimethyl-7-oxa-undecane) urea	4.65
Urea	10.08

EXAMPLE 2

4,10-Diaza-4,10,10-trimethyl-7-oxa-undecane urea

The mixture from Example 1 was dissolved in ether and filtered through silica gel. The silica gel was washed with methanol and the extract was concentrated using a rotary evaporator. Quantitative ^{13}C NMR analysis of the methanol extract is shown in Table 2.

Table 2

Reaction Product Example 2	mole %
4,10-Diaza-4,10,10-trimethyl-7-oxa-undecane urea	89.32
N,N'-Bis-(4,10-diaza-4,10,10-trimethyl-7-oxa-undecane) urea	2.91
Urea	7.77

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EXAMPLE 3

N,N'-Bis-(4,10-diaza-4,10,10-trimethyl-7-oxa-undecane) urea

A one liter 3 neck round bottom flask was fitted with the following: mechanical stirrer, reflux condenser, nitrogen sparger, and a temperature controlled heating mantle. The flask was charged with 8.88 g of urea (CH_4N_2O) and 63.03 g of 4,10-diaza-4,10,10-trimethyl-7-oxa-undecanamine (IV) ($C_{10}H_{25}N_3O$). The mixture was stirred at a constant rate while being slowly heated to 120°C. The reaction was controlled at 120°C until all signs of NH_3 evolution had ceased (as evidenced by bubbling in the N_2 pressure relief device). The temperature was increased to 140°C, 160°C, and 180°C , allowing bubbling to subside between temperature increases. The yellow liquid was cooled to 80 °C and the flask containing the liquid was evacuated via vacuum pump and refilled with N_2 three times to remove any volatiles still present. Quantitative ^{13}C NMR results of the reaction product are presented in Table 3.

Table 3

Reaction Product Example 3	mole %
4,10-Diaza-4,10,10-trimethyl-7-oxa-undecane urea	4.76
N,N'-Bis-(4,10-diaza-4,10,10-trimethyl-7-oxa-undecane) urea	95.24
Urea	0

EXAMPLE 4

In this example a polyurethane foam was prepared in a conventional manner. The polyurethane formulation in parts by weight (pbw):

COMPONENT	PARTS
E-648	60
E-519	40
DC-5043	1.5
Diethanolamine	1.49
Water	3.5
TDI 80	105 Index

E-648 -- a conventional, ethylene oxide tipped polyether polyol marketed by Arco Chemical Co.
E-519 -- a styrene-acrylonitrile copolymer filled polyether polyol marketed by Arco Chemical Co.
DABCO® DC-5043 silicone surfactant marketed by Air Products and Chemicals, Inc.
TDI 80 -- a mixture of 80 wt% 2,4-TDI and 20 wt% 2,6-TDI

For each foam, the catalyst (Table 4) was added to 202 g of the above premix in a 32 oz (951 ml) paper cup and the formulation was mixed for 20 seconds at 5000 RPM using an overhead stirrer fitted with a 2 in (5.1 cm) diameter stirring paddle. Sufficient TDI 80 was added to make a 105 index foam [index = (mole NCO/mole active hydrogen) x 100] and the formulation was mixed well for 5 seconds using the same overhead stirrer. The 32 oz (951 ml) cup was dropped through a hole in the bottom of a 128 oz (3804 ml) paper cup placed on a stand. The hole was sized to catch the lip of the smaller cup. The total volume of the foam container was 160 oz (4755 ml). Foams approximated this volume at the end of the foam forming process. Maximum foam height and time to reach the top of the mixing cup (TOC1) and the top of the 128 oz. cup (TOC2) were recorded (see Table 4).

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Table 4

CATALYSTS	TOC1 (sec)	TOC 2 (sec)	Full Height (sec)	Foam Height (mm)
0.25 pphp DABCO 33LV / 0.10 pphp DABCO BL-11	13.39	41.13	130.04	418.87
0.25 pphp DABCO 33LV	20.54	72.94	192.77	403.10
0.25 pphp DABCO 33LV / 0.18 pphp Ex 1 catalyst	13.75	39.68	117.49	422.92
DABCO 33LV® catalyst -- 33 wt% TEDA in dipropylene glycol from Air Products and Chemicals, Inc. DABCO BL-11 catalyst - 70 wt% bisdimethylaminoethyl ether in dipropylene glycol from Air Products and Chemicals, Inc..				

The data in Table 4 show that the use of the Example 1 catalyst composition afforded an initial reactivity profile as measured by TOC1 and TOC2 comparable to that of the control catalyst BL-11, with the added advantage that full foam height was reached more rapidly. The 33LV only control demonstrated that both the control blowing catalyst BL-11 and the Example 1 blowing catalyst contributed observable catalytic activity at the chosen use levels.

EXAMPLE 5

N,N,N'-Trimethylbis(aminoethyl) ether (TMAEE)

A 2-liter stainless steel autoclave was charged with 499.4 g (3.75 moles) of dimethylaminoethoxyethanol (DMAEE) and 37.9 g of $Cu/ZnO/Al_2O_3$ catalyst. After purging the reactor with N_2 and H_2, the catalyst was reduced in situ under 56 bar of H_2 at a temperature of 195°C for 9 hr. The reactor was then cooled to 25°C and vented to ambient pressure. From a sample cylinder connected to a port in the reactor head, 177 g (5.7 moles) of monomethylamine (MMA) was charged using a 6.5 bar N_2 head to assist in the transfer. After resealing the reactor and pressurizing it to 14.8 bar with H_2, the reactor was heated to 195°C and kept at that temperature for 23.3 hr. The reactor was then cooled to 25°C and 600.1 g of reaction product was recovered after filtration to remove the catalyst particles. Gas chromatographic analysis showed that 65% of the DMAEE was converted and the reaction product contained:

Reaction Product	
	wt%
N,N,N'-trimethylbis(aminoethyl)ether	38.2
Dimethylaminoethoxyethanol	29.4
Water	7.1
Monomethyl amine	5.8
Other amines	19.5

The reaction product was heated under vacuum to remove the low boiling components. A short path distillation was then done to remove heavies and any traces of $Cu/ZnO/Al_2O_3$ catalyst. The overhead product from the short-path distillation (325.6 g) contained:

Overhead Product from Short-Path Distillation	
	wt%
N,N,N'-trimethylbis(aminoethyl)ether	57.2
Dimethylaminoethoxyethanol	37.4

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(continued)

Overhead Product from Short-Path Distillation	
	wt%
Other amines	5.4

This overhead product was used in the preparation of TMCEAEE in Example 6 below.

EXAMPLE 6

N,N,N'-Trimethyl-N'-2-cyanoethylbis(aminoethyl) ether (TMCEAEE)

Into a three necked round bottom flask equipped with a teflon coated magnetic stir bar, reflux condenser, pressure equalizing dropping funnel, and thermometer was placed 325g of the mixture from Example 1 (1.27 moles of contained N,N,N'-trimethylbis(aminoethyl) ether). The mixture was heated to 55°C and 71 g (1.34 moles) of acrylonitrile was added over a period of two hours. The reaction was allowed to proceed an additional five hours until less than 1% of unreacted N,N',N'-trimethylbis(aminoethyl) ether remained. The crude product was used without purification in Example 7.

EXAMPLE 7

4,10-Diaza-4,10,10-trimethyl-7-oxa-undecanamine [N,N,N'-Trimethyl-N'-3-aminopropylbis(aminoethyl) ether (TMAPAEE)]

Into a 1 liter stainless steel autoclave was placed 20g of chromium promoted sponge nickel and 150g of 28% aqueous ammonium hydroxide. The reaction vessel was sealed and purged with nitrogen then hydrogen. The contents of the reaction vessel were then heated to 90°C and the pressure adjusted to 82 bars with hydrogen. Then 426g of the mixture from Example 2 was pumped into the reaction vessel over a period of 3.5 hours. The reaction was allowed to proceed an additional 50 minutes during which time less than 1% of the total hydrogen used was consumed. The hydrogen pressure was maintained at 82 bars throughout the reaction by admission of hydrogen from a 3.79 liter ballast on demand from a dome regulator. The reaction vessel was then cooled and vented and the contents filtered through a 0.45 micron fritted stainless steel filter.

The crude product was placed into a one liter flask and distilled through a 91.4 cm x 2.54 cm i.d. packed column to afford 184.5g of 97.5% pure 4,10-diaza-4,10,10-trimethyl-7-oxa-undecanamine (IV) collected at 124 to 133°C at 13 millibar.

STATEMENT OF INDUSTRIAL APPLICATION

The present invention provides a catalyst composition for preparing polyurethane products, especially polyurethane foams.

Claims

1. 4,10-Diaza-4,10,10-trimethyl-7-oxa-undecane urea.

2. N,N'-Bis-(4,10-diaza-4,10,10-trimethyl-7-oxa-undecane) urea.

3. A catalyst composition comprising compound **I** or compound **II**, or a mixture of compounds **I** and **II**

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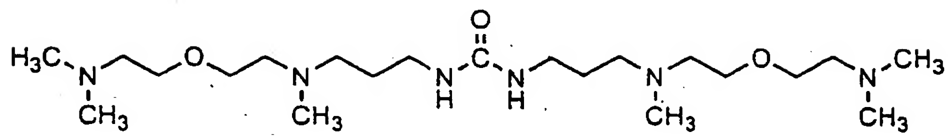

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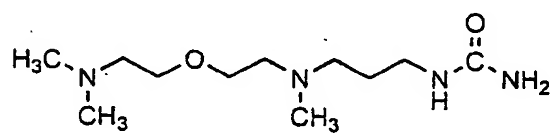

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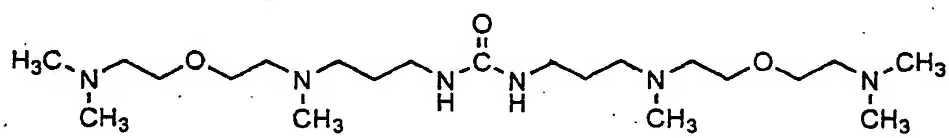
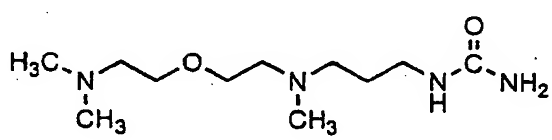
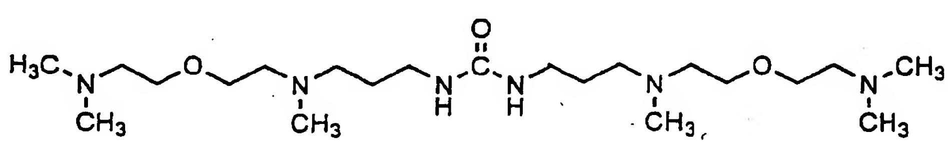
4. The catalyst composition of Claim 3 which comprises

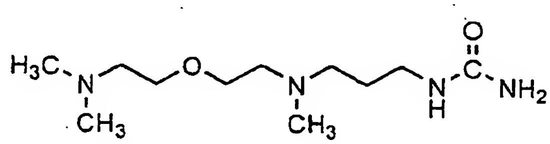


5. The catalyst composition of Claim 3 which comprises



6. The catalyst composition of Claim 3 which comprises a mixture of





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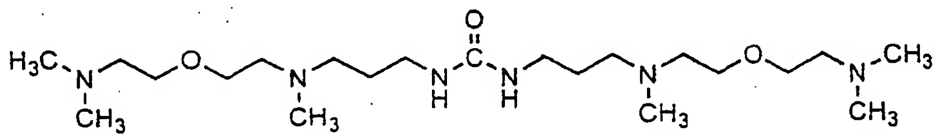
7. A method for catalyzing the trimerization of an isocyanate and/or the reaction between an isocyanate and a compound containing a reactive hydrogen characterized by using a catalyst composition consisting essentially of compound **I** or compound **II**, or a mixture of compounds **I** and **II**



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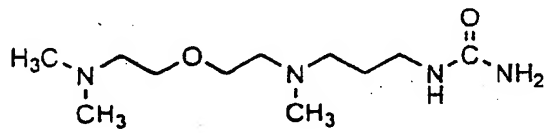

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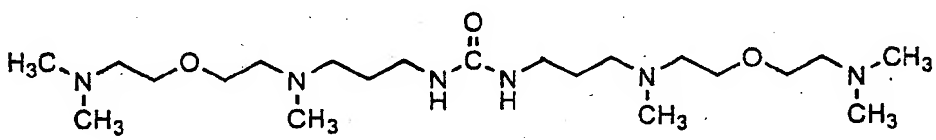
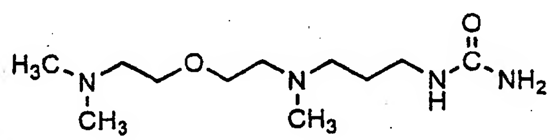
8. The method of Claim 7 in which the catalyst composition comprises



9. The method of Claim 7 in which the catalyst composition comprises



10. The method of Claim 7 in which catalyst composition comprises a mixture of

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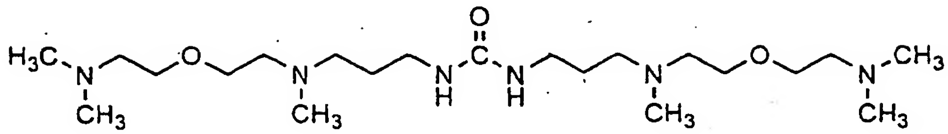

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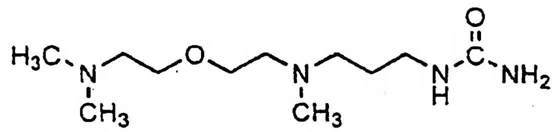
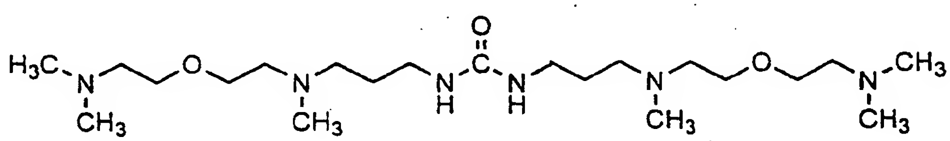
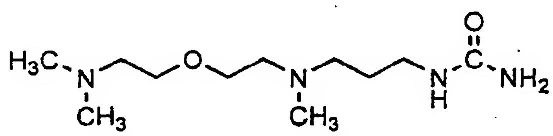


11. A method for preparing a polyurethane foam which comprises reacting an organic polyisocyanate and a polyol in the presence of a blowing agent, a cell stabilizer and a catalyst composition consisting essentially of a gelling catalyst and a blowing catalyst comprising compound I or compound II, or a mixture of compounds I and II

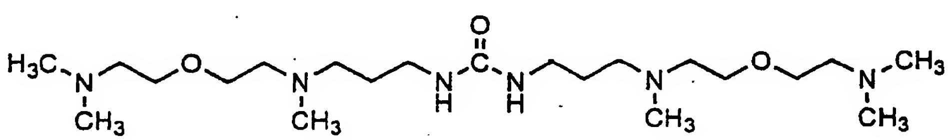


I

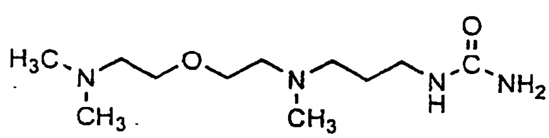


II

12. The method of Claim 11 in which the blowing catalyst comprises



13. The method of Claim 11 in which the blowing catalyst comprises



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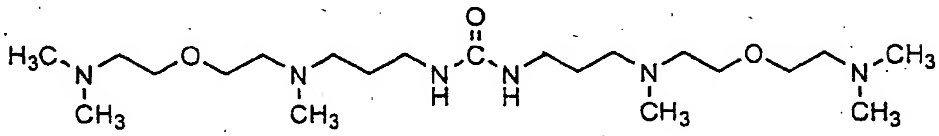
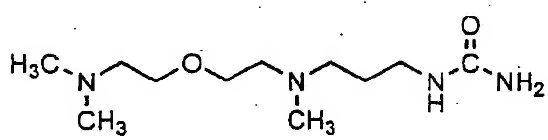
14. The method of Claim 11 in which the blowing catalyst comprises a mixture of



and



BNSDOCID: <EP________0877016A1_I_>

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 7857

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	DE 30 27 796 A (BAYER AG) 18 February 1982 * page 3, line 9 - page 17, line 18 * ---	2,3,7,11	C07C275/10 C07C275/14 C08G18/18
D,A	US 4 194 069 A (SPERANZA GEORGE P ET AL) 18 March 1980 * column 1, line 7 - column 5, line 37 * * example IV; table I * ---	2,3,7,11	
A	US 4 338 408 A (ZIMMERMAN ROBERT L ET AL) 6 July 1982 * column 1, line 17 - column 3, line 63 * * examples I,III * -----	11	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C07C
C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 July 1998	Neugebauer, U

CATEGORY OF CITED DOCUMENTS

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